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**SOLUBILITY AND DIFFUSION STUDIES
OF ULTRA PURE TRANSITION ELEMENTS IN
ULTRA PURE ALKALI METALS

FOURTH QUARTERLY REPORT
(March 29, 1964 – June 27, 1964)**

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SOLUBILITY AND DIFFUSION STUDIES OF ULTRA
PURE TRANSITION ELEMENTS AND COMPOUNDS IN ULTRA PURE
ALKALI METALS

by R. L. McKisson, R. L. Eichelberger,
G. R. Argue, and J. M. Scarborough

I. INTRODUCTION

The purposes of this study are: 1) to define the solution process and determine the equilibrium solubility of highly purified transition metals and selected compounds in highly purified liquid alkali metals, and 2) to measure the diffusion of transition metals and constituents of selected compounds in highly purified liquid alkali metals. The material combinations which are to be considered for both the solution and diffusion studies are: iron, niobium, tantalum, molybdenum, tungsten, zirconium, rhenium, vanadium, hafnium, beryllium oxide, niobium monoxide, tantalum monoxide, zirconium dioxide, zirconium carbide, vanadium monoxide, oxygen-saturated zirconium, and oxygen-saturated hafnium with liquid potassium, and niobium and beryllium oxide with liquid lithium. Specific combinations from the above list will be selected, and it is expected that some combinations will not be investigated.

The studies to be made include the measurement of solubility in the alkali metal at temperatures up to 1200°C, coupled with the investigation of the rate-controlling step and its energy of activation; and the measurement of the liquid state diffusion rate and its energy of activation, also to 1200°C.

It is the goal of this study to develop solubility and diffusion data for well-characterized experimental systems, in which the number and range of complicating variables are minimized, in the hope that such data will not only further

the understanding of these processes in alkali metal systems, but will also be of use in the materials selection and design of space electrical power system components.

This program is divided into the six self-explanatory tasks listed below:

- Task A. Environmental Test System Design and Procurement
- Task B. Material Procurement and Characterization
- Task C. Auxiliary Equipment Design and Procurement
- Task D. Chemical Analysis
- Task E. Experimental Testing and Data Analysis
- Task F. Program Coordination

II. SUMMARY

The environmental test system has been delivered and accepted. Some modifications to the system have been made to improve its performance.

All of the purchased auxiliary equipment has been delivered and assembled into functioning test components. The fabrication of the potassium purification unit has been delayed, and is now scheduled for completion by July 15, 1964.

Two single crystals each of niobium, molybdenum, and tantalum are in the process of electrochemical machining to form single crystal crucibles. Some difficulties have been encountered in the processing but the supplier expects to be able to overcome them. Three additional single crystals of molybdenum were received from Metals Research, Ltd. but their diameters are too small for our use. These crystals have been returned. Replacement of these crystals and the delivery of three niobium single crystals is expected. Two high purity iron crucibles are being prepared for use in the first series of solubility tests.

Chemical analysis techniques for determining the impurities in sample materials have been tested. Verifications of these techniques at the low impurity levels expected in the single crystal materials has proven to be troublesome in that these crystals are in many cases purer than the usual reference standards.

III. TECHNICAL PROGRAM

Environmental Test System

The environmental test system was delivered on April 21, 1964, and was tested for acceptance as per the performance specifications noted on the purchase order. Prior to delivery, all components had met the vacuum specifications when tested in the D. L. Herring Corporation shop. (On July 1, 1964 the D. L. Herring Corporation will change its name to Vacuum/Atmospheres Corporation, VAC.) A summary of these specifications, and the corresponding observed data, are shown in Table I, for the acceptance tests performed at Atomics International.

Following the vacuum-level checkout, the chambers were opened and the various accessories were installed in chambers 1, 2, and 3. A re-check of the vacuum performance was made with very satisfactory results. Vacuum levels in the middle 10^{-7} Torr range were obtained using only the water-baffles.

The automatic liquid nitrogen filling sub-system supplied with the environmental test system proved to be inadequate in that its liquid nitrogen use rate is about 15 liters per hour. The sub system is being modified by the use of more effective insulation and by a change in the method of operation in an attempt to reduce the use rate by a factor of three.

In another modification to the system, the two-inch diffusion pump used with antechamber 1 has been replaced with a four-inch pump to increase the overall pumping speed of that assembly. The system as presently operating is satisfactory, but still has a longer-than-desired

TABLE I

Environmental Test System Acceptance Test Results

Chambers, Ante-chambers	Specification		Best Vacuum Observed***	Pump-down time
	"Ultimate" Vacuum*	Pump-down time**		
C-1	1×10^{-7} Torr	1 hr.	8×10^{-8} Torr	15 min.
C-2	"	"	9×10^{-8} Torr	12 min.
C-3	"	"	7×10^{-8} Torr	15 min.
C-4	"	"	5.5×10^{-8} Torr	16 min.
C-5****	5×10^{-6} Torr	-	2×10^{-7} Torr	-
AC-1	1×10^{-6} Torr	-	1×10^{-6} Torr	-
AC-5	"	-	6×10^{-7} Torr	-

*The vacuum level to be reached after normal outgassing and pumping using the liquid nitrogen cold trap, in a clean, dry, and empty chamber.

**Maximum time to pump from 1 atm to 1×10^{-6} Torr (using a hot diffusion pump).

***These figures are not "ultimate" vacuum levels, but are those read for each chamber during the acceptance tests. All chambers in which pumping was continued after completion of the acceptance tests achieved lower vacuum levels.

****C-5 is the mercury diffusion pumped chamber. Its vacuum level specification was based upon manufacturer's data, but the system performs significantly better than their expectations.

pump-down time. Further reduction in pump-down time will require increasing the vacuum line conductance, and will be deferred until the experimental program is well underway.

All of the purchased environmental test system components have been delivered and are installed. It is particularly satisfying to observe that the operation of the CVC Type SR-75 rotary seals does not affect the vacuum level in chamber 2. The incremental loss in vacuum produced by the operation of these seals is $1-2 \times 10^{-7}$ Torr.

The RYE Controls Model MIHT manipulators have been found to have only a minor effect on the vacuum level when they are at rest, and values of $1-2 \times 10^{-7}$ Torr are readily maintained. In use, however, they do introduce gas into the system and the vacuum reading rises to the high 10^{-7} or low 10^{-6} Torr range. Vacuum recovery to the low 10^{-7} Torr range is observed within 30 seconds after the manipulators are placed at rest.

Figure 1 shows a view of the environmental test system from the working platform with some of the components labelled. Figure 2 shows a view of the welding work station with the welding power console, the gun, and the view port, as indicated. Figure 3 shows a view of the inside of chamber 3 with the test furnace and chill block open.

The 24-point recorder and the two furnace controllers have been installed in their control consoles. The two furnace control systems are now complete, the temperature sensing and recording system console with the multipoint recorder is complete, and the power console for use with the potassium purification unit is complete.

The potassium purification unit fabrication and assembly fell behind schedule due to priority scheduling in the machine shops. The parts were re-scheduled for release on June 12, and were delivered on

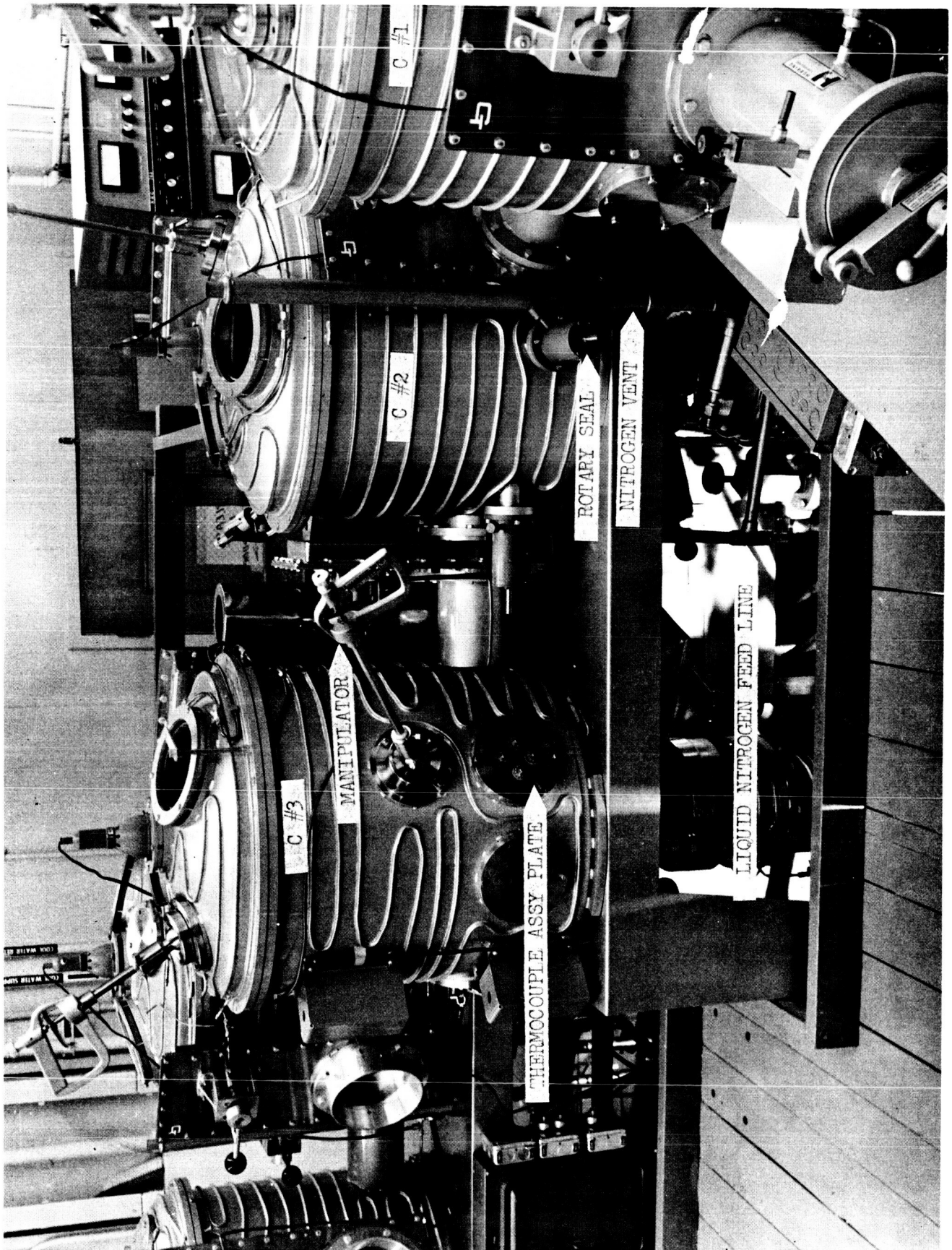


FIGURE 1. ENVIRONMENTAL TEST SYSTEM

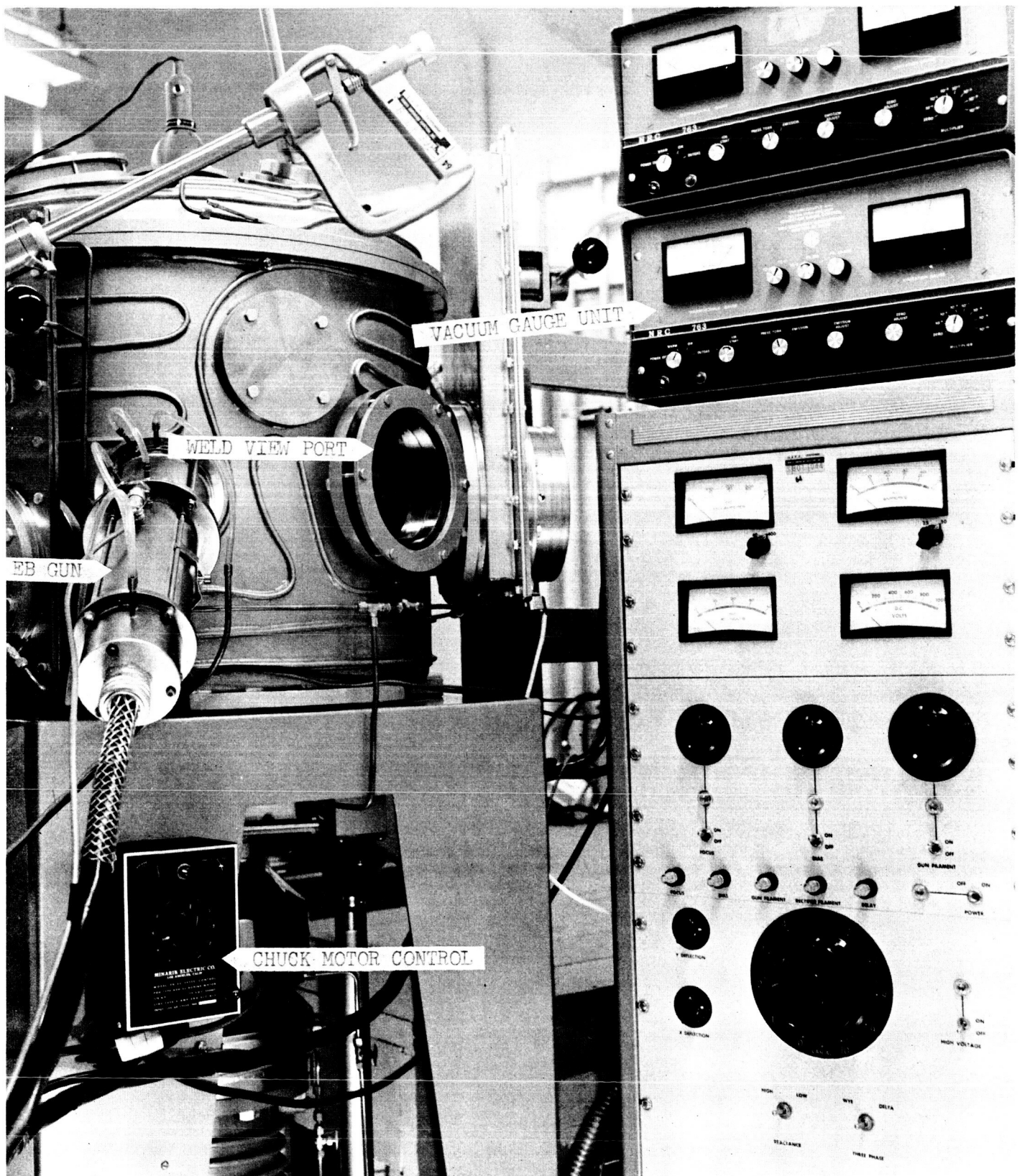


FIGURE 2. WELDING STATION

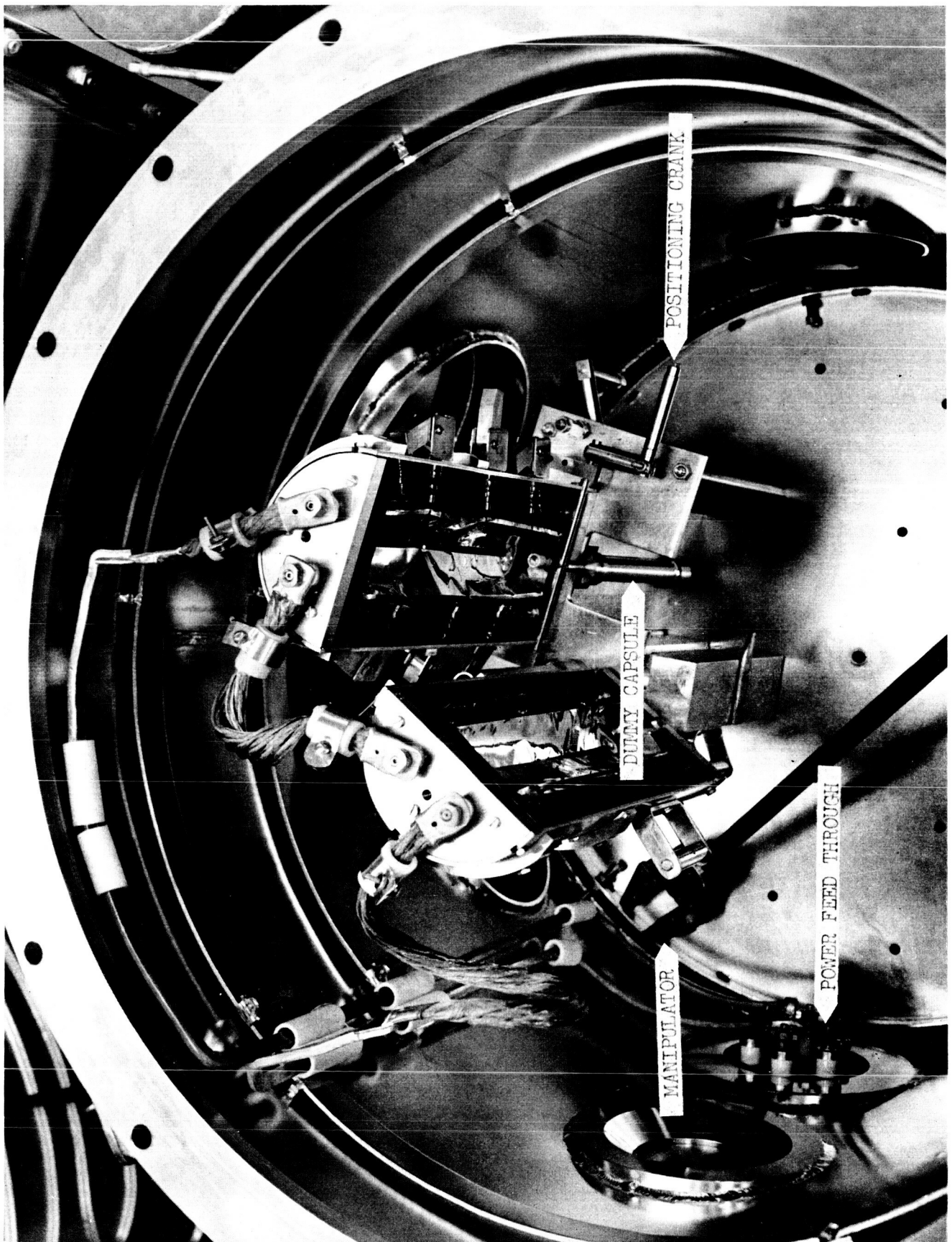


FIGURE 3. FURNACE AND CHILL BLOCK ASSEMBLY, CHAMBER #3.

June 19. The assembly and the installation of the heaters, and of the sensing and control thermocouples, are in progress. Completion is now expected by July 15, at which time the first potassium-fill and unit-seasoning operation will be carried out. Figure 4 shows the partly completed unit with the heaters and the thermocouples partially installed.

Material Procurement, Preparation, and Characterization

Six refractory metal single crystals (two each of Mo, Ta, and Nb) were delivered to Sifco Metachemical in Cleveland for electrochemical machining. These crystals are nominally one-half inch in diameter and three inches long. Sifco will electrochemically machine a nominal 3/8-inch diameter hole, 2-1/2 inches deep in the niobium and molybdenum crystals.

Some reduction of hole size will be necessary to obtain crucibles from the tantalum crystals, which are not straight, but the crucibles of Nb and Mo were expected to offer no difficulties. However, none of the crucibles has yet been delivered. Sifco reports that the single crystal materials react quite differently in their processing than do the polycrystalline refractory metals. They are therefore modifying their processing variables in an attempt to improve the process' performance on the single crystals.

Two high purity polycrystalline iron samples have been machined to form solute crucibles. Their internal surfaces are being electropolished and then the internal areas will be measured using the DLC technique.

Three molybdenum single crystals were received from Metals Research, Ltd. (England). The specification on these called for an 0.45 inch minimum diameter, but the crystals were typically 0.35-0.40 inches in diameter and not usable. A telephone conversation with the MR agent regarding these undersize parts elicited the comment that they observe a decrease in crystal diameter each time they make a zone-refining pass, but the amount of diameter change is very difficult to predict and control. The undersized crystals were sent in the belief that the

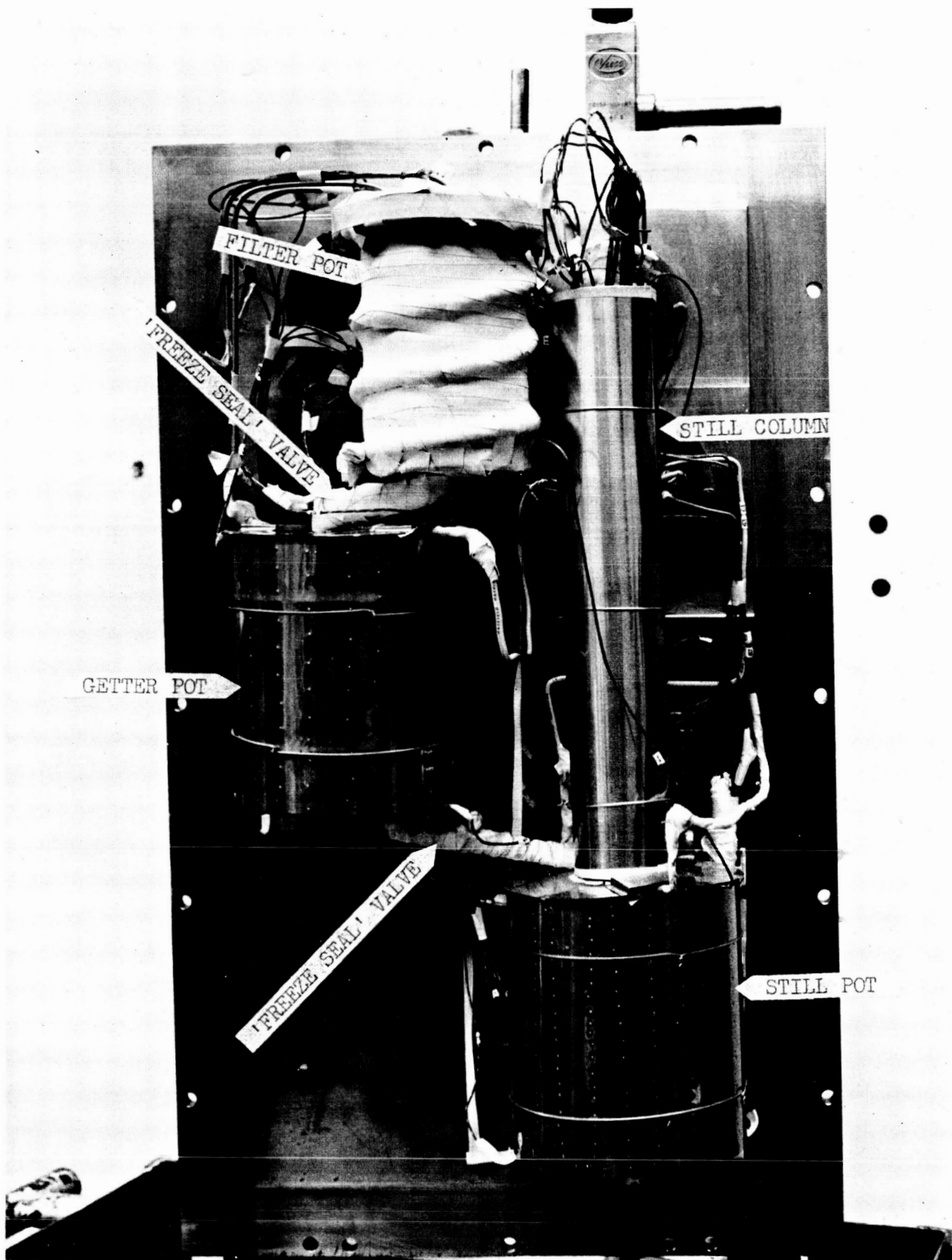


FIGURE 4. POTASSIUM PURIFICATION UNIT, DURING ASSEMBLY

diameter was not a critical factor. We will return two of the undersized molybdenum crystals, and MR will attempt to prepare three more of the required diameter to satisfy the contract.

Metals Research also has an order for three niobium single crystals and three tantalum single crystals. They have prepared two of the niobium crystals which are reported to be of the required size and are working on the third. They have not yet begun the preparation of the tantalum crystals and are no longer certain that they can achieve an 0.45-inch diameter product.

Further studies of the double layer capacitance (DLC) method of determining surface areas have been made. Samples of the high purity polycrystalline iron were tested. Mechanically polished surfaces gave values of DLC ranging from five to seven microfarads/sq. cm. The variance is most probably caused by the minute differences in the natures of different polished surfaces. The electropolished surface measurements were reproducible, provided the test voltage was varied beginning at the cathodic end of the emf vs. capacity curve. These measured values of DLC are ten microfarads/sq. cm. When the emf sweep is made from the anodic end, a surface reaction of a variable intensity occurs which leads to the observation of erratic DLC values. The layer formed by the cathodic-to-anodic sweeps is quite reproducible, and the surface area is readily measured on this basis.

Auxiliary Equipment

The outgassing furnace has been installed in chamber 1 and performed well in a 500°C test. The Variac which feeds power to the step-down transformer was operating at about 50% of full voltage.

A furnace and chill block assembly has been set up in chamber #3 and given a preliminary test. All parts function well except the thermo-couple support and sample contacting sub-assemblies. These are proving to be awkward to adjust using the manipulators. A modification of the operating tool is being made to enable a more positive release of the

weights which apply pressure to hold the thermocouples against the test capsule.

A test weld was made with the electron beam welder in chamber #2 using trial pieces of molybdenum. The operation went smoothly, with the production of a good-looking weld which was helium leak tight. Figure 5 shows a molybdenum cap and dummy capsule section ready to weld, the cut sections of the weld itself, and the top section of the cap which was separated using our cut-off tool. This particular trial weld showed the effects of too low a voltage (shallow penetration) and too high a current (wide melt zone), but nevertheless served to prove that the weld unit operates very satisfactorily. Transfer of parts into the system through the antechamber, and the manipulator operations needed for the welding proved to be convenient and efficient.

The external "hard-vacuum" high temperature outgassing furnace has been set up and is in operation. It consists of a cold-trapped two-inch oil diffusion pump system made of three-inch Pyrex pipe. Three current concentrators have been made and tested. One is used to outgas the capsule bodies; the second is used for the capsule caps, and the third is used for the sample collectors and will be used with the crucibles. The procedure used is quite straightforward. The piece to be outgassed is placed in its current concentrator and the system evacuated. The molybdenum parts are heated to 1800-1900°C and held at temperature until the vacuum level falls below 2×10^{-6} Torr. Tantalum sample collectors are heated to 2000-2100°C and held at temperature until the vacuum falls below 2×10^{-6} Torr. In general, the cycle takes about four hours.

A test of the furnace control system was made using a dummy test capsule. The response time of the controller, and its ability to follow demands imposed by manually altering the set point were quite satisfactory. A "sample" temperature of 1200°C was obtained using only 50% of the available power. This indicates the power supply to be over-designed, but since the control system functions well at the low-power end of its



FIGURE 5. ELECTRON BEAM TEST WELD

service range, no difficulties are expected. The obvious advantage is that the furnaces can achieve temperatures well over the design value of 1200°C.

Chemical Analyses

The analytical chemistry support effort requires the determination of the solute metals in potassium at low levels with high precision, and the verification of purity of the solvent potassium and solute metals. During this quarter, methods have been verified for determining the solutes Fe, Mo, W, Re, and V in a potassium matrix in the 1 to 10 ppm range. Similar verification is nearly complete for Nb, Ta, Zr, and Hf. Thus, analytical methods for determining all the solute metals to be investigated in the solubility program appear to be satisfactory.

The status of the analytical chemistry effort to determine the impurities present in the ultra-pure potassium which will be prepared by the project is shown in Table 2. Again, work in this laboratory has been adequate to demonstrate that methods are available here for the analyses needed.

The situation is not so favorable in regard to the determination of impurities in refractory metal crucible materials. As expected, the analysis for elements present in the few ppm range in the refractory metals proves difficult. Niobium and silicon, for example, interfere with one another when both are present as impurities in, say, tantalum. The analysis for niobium is also complicated by the presence of tantalum, and by molybdenum.

An attempt was made to set up an exchange column to effect the separation of interfering elements, but it was generally unsuccessful. One of the two principal problems encountered results from the "tailing" of the major component during the elution of the minor impurities from the ion exchange columns. The other problem involves the recovery of microgram quantities of impurities from large volumes of elutriant solutions. Although both of these problems can probably be solved, the effort required is not consistent with the present scope of the

analytical support program. Several additional experiments are planned, however, in order to verify these conclusions.

Chemical verification of the vendor's typical analysis for iron in the single crystal refractory metals has been completed, however. Table 3 shows the concentrations of iron found in the six crystals, using a colorimetric method with batho-phenanthroline.

Spectrographic analysis for silicon has shown less than 10 ppm in the molybdenum. A figure of 150 ± 75 ppm silicon has tentatively been found for the tantalum sample, but better standards are needed before this value can be accepted.

An analysis for impurities in the iron crucible materials was carried out. The vendor's analysis shows the presence of copper, magnesium, molybdenum and silicon (at the 1 ppm level). Our qualitative spectrographic analysis confirms the presence of Mg and Si, and indicates that manganese is also present. An attempt to verify chemically the presence of Cu and Mo, which were not found spectrographically at AI, is planned. Verification of the permanganate method for manganese was completed, and an analysis of the iron sample showed that it contains less than 0.5 ppm Mn. The biquinoline method for determining copper in iron has been verified in the region of 1 to 10 ppm. The thiocyanate method for molybdenum was tested and found to be satisfactory. An alternate method based on the extraction of molybdenum with 8-hydroxyquinoline is being evaluated.

TABLE 2

The Determination of Impurities in Potassium

<u>Impurity and Method of Analysis</u>	<u>Status</u>
Oxygen (Mercury Amalgamation)	Equipment and procedure tested using sodium at the 15 ppm level, precision is $\pm 2.5 \mu\text{g}$. Improvement in accuracy and precision is anticipated.
Nitrogen (Colorimetric-Nessler's Reagent)	Procedure verified using sodium. Range 1 - 5 ± 0.2 ppm.
Carbon (Wet oxidation-Van Slyke Reagent)	Accuracy and sensitivity limited by reproducibility of the reagent blank which is good to $\pm 5 \mu\text{g}$ of elemental carbon. Improvement in blank values anticipated.
Phosphorous (Colorimetric-Molybdenum blue)	Verified in the presence of potassium to 1.0 ± 0.05 ppm.
Hydrogen (Vacuum Extraction-Manometric plus mass spectrometry)	Procedure available which has been used for determining hydrogen in sodium. Adequate sensitivity to meet requirements.
Sulfur (Colorimetric-p-amino-dimethylaniline)	Procedure has not been verified in a potassium matrix. Sensitivity to 1.0 μg has been demonstrated in other materials.
Other Alkali Metals (Atomic Absorption Spectrophotometry)	Sensitivity to 1 μg is possible.
Other Metallic Impurities including Silicon (Spectrographic)	Sensitivity for impurities is adequate. Standards must be prepared pending qualitative analysis of actual sample.

TABLE 3

Iron Analysis in Refractory Single Crystal Samples

<u>Single Crystal</u>	<u>Iron Found, ppm</u>
Nb-1	11.8 ± 0.3
Nb-2	11.2 ± 0.3
Mo-1	6.0 ± 0.2
Mo-2	5.0 ± 0.2
Ta-1	10.0 ± 0.3
Ta-2	6.0 ± 0.3

IV. NEXT REPORT PERIOD ACTIVITIES

During the next quarter, the remaining unfinished items and the equipment modifications necessary for the initiation of solubility tests will be completed.

The major effort will be directed toward initiating experimental measurements on the polycrystalline iron samples, and on the single crystal niobium, molybdenum, and tantalum samples, as they are delivered from Sifco.

V. REPORTS ISSUED ON THIS CONTRACT

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Quarterly Report, AI-64-5, February 7, 1964.
- R. L. McKisson, R. L. Eichelberger, G. R. Argue, and J. M. Scarborough,
"Solubility and Diffusion Studies in Alkali Metals," Third
Quarterly Report, NASA-CR-54043 (AI-64-75), May 11, 1964.
- G. R. Argue, "Double Layer Capacitance Measurements on Ta, Mo, and
Nb," AI-TDR-9773, March (1964).
- R. L. McKisson, "Analysis of the Freezing Point Depression Technique
of Determining Impurity Content of Alkali Metal," AI-TDR-9404,
(March, 1964).